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(54) Rubber composition for tire treads

Kautschukmischungen für Reifenlaufflächen

Composition de caoutchouc pour bandes de roulement de pneus

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(56) References cited:
DE-A- 4 011 983 **GB-A- 674 011**
US-A- 2 894 926 **US-A- 4 522 970**

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Description

[0001] The present invention relates to rubber compositions for tire treads, and more particularly rubber compositions for tire treads which provide good braking performance and driving stability not only on general roads but also on wet road surfaces of motor race circuits.

[0002] In recent years, as automobiles have become capable of running at higher speeds, requirements imposed on their tire properties have become increasingly severe. Among such properties are performances of tires in operation at a high speed on a wet road surface. In order to improve tire properties including braking performance and driving stability on wet surfaces at high speeds, it is possible to take measures including enhancing the power for gripping the road surface, improving cornering characteristics by increasing the block rigidity of tire tread patterns and thereby resisting deformation at the time of cornering, and preventing a hydro-planing phenomenon by prohibiting deformation of grooves formed in tire treads so that water held in the grooves is discharged smoothly.

[0003] Conventionally, gripping power was enhanced by incorporating silica into high-styrene SBR, which has excellent mechanical characteristics.

[0004] Silica-containing rubber compositions for tire treads can improve gripping power in a low temperature range of 15° C or less. However, they have the drawback that they cannot exhibit successful gripping power on wet road surfaces or on semi-wet (damp) road surfaces in a high temperature range of 15° C or more, in which cooling effect by water is small.

[0005] In addition, if a great amount of silica is incorporated into a rubber composition, silica particles grind an oxide coating of the inner surface of a mixer during kneading, and then rubber components adhere to the flakes thus produced to reduce operating efficiency.

[0006] Attention is also drawn to the disclosures of DE-A-4 011 983, US-A-4 522 970, and US-A-2 894 926.

[0007] In view of the foregoing, an object of the present invention is to provide a rubber composition for tire treads which enhances gripping power on wet and semi-wet road surfaces which are not only in a low temperature range but also in a high temperature range, and which enhances operating efficiency during manufacture of the composition.

[0008] Accordingly, the present invention provides a rubber composition for tire treads characterized by comprising a rubber component containing at least 70 parts by weight of a styrene-butadiene rubber whose styrene content is 20 to 60% (the unit of the styrene content is % by weight throughout in the specification and claims); and further comprising, based on 100 parts by weight of the rubber component:

5 to 150 parts by weight of a powdery inorganic compound represented by the following formula (I) and having a particle size from 0.01 to 10 μm :



in which M^1 is at least one selected from the group consisting of Al, Mg, Ti, and Ca; any oxide of any one of the metals; or any hydroxide of any one of the metals; and m, x, y, and z are integers from 1 to 5, 0 to 10, 2 to 5, and 0 to 10, respectively;

5 to 170 parts by weight of carbon black having a nitrogen adsorption specific area of 80 to 280 m^2/g so that the total amount of the powdery inorganic compound and the carbon black falls in the range of 70 to 200 parts by weight; 5 to 100 parts by weight of silica having a nitrogen adsorption specific area of 130 to 280 M^2/g , wherein the total amount of the powdery inorganic compound and the silica and the carbon black falls in the range of 80 to 250 parts by weight based on 100 parts by weight of the overall rubber component;

the amount of an extract obtained by extracting the rubber composition after being vulcanized from acetone and chloroform being 30 to 270 parts by weight, based on 100 parts by weight of the rubber component.

[0009] In the following description, reference will be made to the accompanying drawing, wherein Fig. 1 is a sectional view showing a main portion of a road surface friction tester used in the road surface friction test in the present invention.

[0010] The rubber component which is used in the present invention comprises a styrene-butadiene rubber having a styrene content of 20 to 60%. If the styrene content is less than 20%, desired gripping power cannot be obtained in the above-mentioned low temperature range nor high temperature range. If the styrene content is in excess of 60%, block rigidity becomes unnecessarily high to reduce the amount of bite of the rubber into a road surface, and desired gripping power cannot be obtained. In order to obtain significant advantages, it is preferred that the styrene content be from 30 to 45%. The styrene-butadiene rubber can be prepared by any synthesis method such as emulsion polymerization or solution polymerization.

[0011] The rubber component which is used in the present invention may include other rubber component(s) in

addition to the above-mentioned styrene-butadiene rubber. Examples of such other rubber component(s) include, but are not limited to, cis-1,4-polyisoprene, low cis-1,4-polybutadiene, high cis-1,4-polybutadiene, ethylene-propylene-diene rubbers, chloroprene, halogenated butyl rubbers, acrylonitrile-butadiene rubbers, and natural rubbers. Styrene-butadiene rubbers with a styrene content falling outside the range described above may be used as the "other rubber component(s)". One or more species of the "other rubber component(s)" may be included in the rubber components used in the present invention.

[0012] A styrene-butadiene rubber containing styrene in an amount within the above-described range is present in an amount of not less than 70 parts by weight per 100 parts by weight of the overall rubber components used in the present invention. If the amount of styrene-butadiene rubber is less than 70 parts by weight, desired gripping power cannot be obtained both in low and high temperature ranges.

[0013] The rubber composition for tire treads of the present invention comprises a powdery inorganic compound represented by the following formula (I):



in which M^1 is at least one metal selected from the group consisting of Al, Mg, Ti, and Ca; any oxide of any one of the metals; or any hydroxide of any one of the metals; and m, x, y, and z are integers from 1 to 5, 0 to 10, 2 to 5, and 0 to 10, respectively.

[0014] In formula (I), when x and z are both 0, the inorganic compound is at least one selected from the group consisting of Al, Mg, Ti, and Ca; metal oxides thereof, or metal hydroxides thereof.

[0015] Examples of the inorganic compounds of formula (I) include alumina (Al_2O_3), aluminum hydroxide [$Al(OH)_3$], magnesium hydroxide [$Mg(OH)_2$], magnesium oxide (MgO), talc ($3MgO \cdot 4SiO_2 \cdot H_2O$), attapulgite ($5MgO \cdot 8SiO_2 \cdot 9H_2O$), titanium white (TiO_2), titanium black (TiO_{2n-1}), calcium oxide (CaO), calcium hydroxide [$Ca(OH)_2$], magnesium aluminum oxide ($MgO \cdot Al_2O_3$), clay ($Al_2O_3 \cdot 2SiO_2$), kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$), bentonite ($Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$), aluminium silicate (for example, Al_2SiO_5 , $Al_4 \cdot 3SiO_4 \cdot 5H_2O$), magnesium silicate (for example, $Mg_2 \cdot SiO_4$, $MgSiO_3$), calcium silicate ($Ca_2 \cdot SiO_4$), calcium aluminium silicate (for example, $Al_2O_3 \cdot CaO \cdot 2SiO_2$), and calcium magnesium silicate ($CaMgSiO_4$).

[0016] The above-mentioned aluminum hydroxide includes alumina hydrates ($Al_2O_3 \cdot 3H_2O$).

[0017] These inorganic compounds represented by formula (I) may be used singly or in combination of two or more. Among them, aluminum hydroxide is particularly preferred in view of its advantage of prominently enhancing the gripping power.

[0018] The above-described inorganic compounds must be in the form of a powder with a particle size of 0.01-10 μm . If the inorganic compounds have a particle size of less than 0.01 μm , operating efficiency in kneading is reduced while enhanced gripping power is not expected. A particle size in excess of 10 μm is not suitable, either, since the modulus of elasticity greatly decreases and in addition sufficient gripping power is not obtained even at the sacrifice of abrasion resistance. In order to obtain advantageous effects at a high and well-balanced level, the particle size is preferably from 0.05 to 5 μm and more preferably from 0.1 to 3 μm .

[0019] The rubber composition for tire treads according to the present invention contains carbon black with a nitrogen adsorption specific area (N_2SA) of 80 to 280 m^2/g . A nitrogen adsorption specific area of less than 80 m^2/g is not suitable because an appropriate modulus of elasticity and sufficient gripping power cannot be obtained, and in addition, abrasion resistance becomes poor. A nitrogen adsorption specific area in excess of 280 m^2/g is not suitable either, because operating efficiency in kneading decreases.

[0020] Examples of the carbon black which can be used in the present invention include N330, N220, and N110 (according to the designation of ASTM, which are otherwise abbreviated as HAF, ISAF, and SAF in Japan). Among them, N110 is preferable from the viewpoint of enhancing gripping power on a wet road surface in a low temperature range, and on a wet or semi-wet road surface in a high temperature range.

[0021] The amounts of the above-mentioned powdery inorganic compound and carbon black are 5-150 parts by weight and 5-170 parts by weight, respectively, per 100 parts by weight of the overall rubber components. In addition, the total amount of the inorganic powder and carbon black is from 70 to 200 parts by weight with respect to 100 parts by weight of the overall rubber components. If the amount of the inorganic powder is less than 5 parts by weight, sufficient gripping power cannot be obtained, which is undesirable. Also, it is not suitable that the amount of inorganic powder be in excess of 150 parts by weight, because sufficient gripping powder is not obtained at the sacrifice of abrasion resistance. If the amount of the carbon black is less than 5 parts by weight, sufficient gripping power is not obtained even at the sacrifice of abrasion resistance, whereas if it is in excess of 170 parts by weight, operating efficiency in kneading drops, which is undesirable. If the total amount of the inorganic powder and carbon black is less than 70 parts by weight, sufficient gripping power is not obtained, whereas if the total amount is in excess of 200 parts by weight, operating efficiency in kneading drops. In order to obtain improved advantageous effects, the amounts of

the inorganic compounds and the carbon black are preferably 15-120 parts by weight and 15-140 parts by weight, respectively, and the total amount of the inorganic compound and carbon black is preferably 70-180 parts by weight.

[0022] The rubber composition for tire treads according to the present invention may contain one or more of C₉ aromatic petroleum resins and alkylphenol resins. In this description, the term "C₉ aromatic petroleum resins" refers to polymers of C₉ aromatic monomers. Examples of the C₉ aromatic monomers include vinyl toluenes, α -methylstyrenes, coumarones, and indenenes. The C₉ aromatic monomers may be used singly or in combination of two or more. Examples of the alkylphenol resins include alkylphenol-acetylene resins such as p-t-butylphenol-acetylene and alkylphenolformaldehyde resins such as cresols, xylenols, p-t-butylphenols, and p-t-octylphenols. The softening point of these resins is preferably from 60 to 150°C. A softening point of lower than 60° C does not yield sufficient gripping power on a wet road surface nor on a semi wet road surface, in a high-temperature range. On the other hand, if the softening point is in excess of 150° C, the resins are not uniformly dispersed when they undergo kneading. Also, operating efficiency in kneading decreases, and abrasion resistance significantly decreases. These C₉ aromatic petroleum resins and alkylphenol resins may be used singly. Alternatively, two or more species of them may be used together. Furthermore, the C₉ aromatic petroleum resins and alkylphenol resins may be used in combination at the same time. Preferred examples of the C₉ aromatic petroleum resins include Neopolymer 80 (trademark, product of Nippon Petrochemical Co., Ltd., softening point=83° C) and Neopolymer 140 (trademark, product of Nippon Petrochemical Co., Ltd., softening point=145° C). Preferred examples of the alkylphenol resins include Phenolite AA1101 (trademark, product of Dainippon Ink and Chemicals, Inc., softening point=94° C).

[0023] The amount of the resin is from 3 to 50 parts by weight with respect to 100 parts by weight of the above-mentioned overall rubber components. If the amount of the resin is less than 3 parts by weight, desired gripping power cannot be obtained, whereas if the amount is in excess of 50 parts by weight, operating efficiency in kneading is significantly reduced. In order to obtain improved advantageous effects, the amount of the resin is preferably 5-40 parts by weight.

[0024] In the present invention, the amount of an extract obtained by extracting the rubber composition from acetone and chloroform after being vulcanized is from 30 to 270 parts by weight with respect to 100 parts by weight of the overall rubber component. It is not suitable that the amount of extract be less than 30 parts by weight or in excess of 270 parts by weight, because, in both cases, operating efficiency in kneading decreases while neither enhanced gripping force or improvement in abrasion resistance can be expected. In order to obtain gripping force, abrasion resistance, and operating efficiency in kneading at a high and well-balanced level, it is preferred that the amount of the extract be from 30 to 200 parts by weight.

[0025] In the rubber composition for tire treads according to the present invention, various additives ordinarily used in the rubber industry may be incorporated in addition to the components described above. Such optional components include vulcanizing agents such as sulfur, various vulcanization-accelerators, various softeners, various anti-aging agents, zinc oxide, stearic acid, aromatic oils, antioxidants, and ozone degradation inhibitors.

[0026] The rubber composition for tire treads according to the present invention also contains silica having a nitrogen adsorption specific area (N₂SA) of 130 to 280 m²/g. It is not suitable that the nitrogen adsorption specific area of silica be less than 130 m²/g, because sufficient modulus in elasticity cannot be obtained. A nitrogen adsorption specific area in excess of 280 m²/g is not suitable, either, because operating efficiency in kneading decreases while enhanced gripping power is not expected.

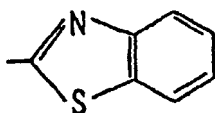
[0027] The type of silica which is used in the present invention is not particularly limited. For example, silica manufactured by a dry process (silicic acid anhydride) and silica manufactured by a wet process (silicic acid hydrate) can be used, of which silica manufactured by a wet process is preferred. Preferred examples of the silica manufactured by a wet process include Nipseal VN3 AQ (trademark, manufactured by Nippon Silica Co.).

[0028] The amounts of the powdery inorganic compound, silica, and carbon black are 5-150 parts by weight, 5-100 parts by weight, and 5-170 parts, respectively, based on 100 parts by weight of the aforementioned overall rubber components. In addition, the total amount of the three is 80-250 parts by weight based on 100 parts by weight of the overall rubber components. If the amount of the powdery inorganic compound is less than 5 parts by weight, sufficient gripping power cannot be obtained, which is undesirable. Also, it is not suitable that the amount of inorganic powder be in excess of 150 parts by weight, because the modulus in elasticity greatly decreases and abrasion resistance becomes poor. If the amount of the silica is less than 5 parts by weight, gripping power on a wet road surface is insufficient, whereas an amount in excess of 100 parts by weight will result in greatly decreased operating efficiency in kneading and no improvement in abrasion resistance. If the amount of the carbon black is less than 5 parts by weight, sufficient reinforcing property is not obtained and abrasion resistance is reduced, whereas if it is in excess of 170 parts by weight, operating efficiency in kneading drops while enhanced gripping power and improvement in abrasion resistance are not expected. Moreover, if the total amount of the powdery inorganic compound, silica, and carbon black is less than 80 parts by weight, sufficient gripping power and abrasion resistance cannot be obtained, whereas if the total amount is in excess of 250 parts by weight, operating efficiency in kneading is reduced while enhanced abrasion resistance cannot be expected. In order to obtain sufficiently advantageous effects, the amounts of the powdery inor-

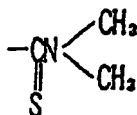
ganic compound, silica, and the carbon black are preferably 15-120 parts by weight, 30-100 parts by weight, and 15-140 parts by weight, respectively, and the total amount of them is preferably 100-230 parts by weight.

[0029] The rubber composition for tire treads according to the present invention may contain 3-20% by weight of a silane coupling agent. Silane coupling agents have an action of intensifying the linkage of silica and rubber components to improve abrasion resistance. It is not suitable that the amount of the silane coupling agent be less than 3% by weight or in excess of 20% by weight based on the amount of the silica, since noticeable effect of the silane coupling agent is not obtained in the former case, and the effect of the coupling agent is not commensurate to the increase in costs in the latter case.

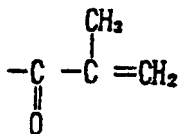
[0030] The silane coupling agents which are suitably used in the present invention are represented by the formula $Y_3-Si-C_nH_{2n}A$, wherein Y is C_1-C_4 alkyl, alkoxy, or a chlorine atom and three Y's may be the same or different from each other, n is an integer from 1 to 6 inclusive, A is $-S_mC_nH_{2n}Si-Y_3$, nitroso, mercapto, amino, epoxy, vinyl, a chlorine atom, imido, and $-S_mZ$ wherein m is an integer from 1 to 6 inclusive, n and Y are as defined hereinabove, and Z is a group selected from the compounds (A), (B), and (C):



(A)



(B)



(C)

[0031] Specific examples of silane coupling agents which are used in the present invention include bis(3-triethoxysilylpropyl)tetrasulfide, bis(2-triethoxysilylethyl)tetrasulfide, bis(3-trimethoxysilylpropyl)tetrasulfide, bis(2-trimethoxysilylethyl)tetrasulfide, 3-mercaptopropyl trimethoxysilane, 3-mercaptopropyl triethoxysilane, 2-mercaptoethyl trimethoxysilane, 2-mercaptoethyl triethoxysilane, 3-nitropropyl trimethoxysilane, 3-nitropropyl triethoxysilane, 3-chloropropyl trimethoxysilane, 3-chloropropyl triethoxysilane, 2-chloroethyl trimethoxysilane, 2-chloroethyl triethoxysilane, 3-trimethoxysilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, 3-triethoxysilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, 2-triethoxysilylethyl-N,N-dimethylthiocarbamoyl tetrasulfide, 3-trimethoxysilylpropylbenzothiazole tetrasulfide, 3-triethoxysilylpropylbenzothiazole tetrasulfide, 3-triethoxysilylpropylmethacrylate monosulfide, and 3-trimethoxysilylpropylmethacrylate monosulfide. In order to achieve a balance between the advantageous effect of silane coupling agent and economy, bis(3-triethoxysilylpropyl)-tetrasulfide, 3-trimethoxysilylpropylbenzothiazole tetrasulfide and the like are preferred. Examples of the silane coupling agents in which three Y's are not the same include bis(3-diethoxymethylsilylpropyl)tetrasulfide, 3-mercaptopropyl dimethoxymethylsilane, 3-nitropropyl dimethoxymethylsilane, 3-chloropropyl dimethoxymethylsilane, dimethoxymethylsilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, and dimethoxymethylsilylpropylbenzothiazole tetrasulfide.

EXAMPLES

[0032] The present invention will next be described in more detail by way of examples, which should not be construed as limiting the invention. However, all the Examples 1A to 7A referred to below are outside the scope of the invention because they do not contain silica.

Examples 1A to 7A and Comparative Examples 1A to 3A:

[0033] The components (amounts expressed as parts by weight) shown in Tables 1 and 2 were kneaded in a Banbury mixer to prepare various rubber compositions for tire treads.

[0034] The obtained rubber compositions for tire treads were vulcanized at 145° C for 45 minutes, after which they were subjected to a variety of measurements described below.

[0035] The styrene content in the styrene-butadiene rubber was determined from the calibration curve of an infrared method based on the absorption of phenyl groups at 699 cm⁻¹.

[0036] Extraction from acetone and chloroform was performed in accordance with JIS K 6350.

[0037] A road surface friction test was performed using a road surface friction tester described in JU-A-5-66545. As shown in Fig. 1, the road surface friction tester 10 is housed in an unillustrated casing which is placed on a road surface 34 formed, for example, of asphalt. The tester is equipped with a frame 32. To the top of the frame 32 is fixed a bellows 31 which is connected to an air source unit (not shown) through an unillustrated air tube. Immediately below the bellows 31, a load cell 30 and a motor 29 are disposed. The load cell 30 detects downward loads applied by the bellows 31 due to the air pressure supplied by the air source unit. The load cell 30 and motor 29 are securely fixed by guide frames 33 so as not to deviate from a position directly beneath the bellows 31, thereby preventing the data from varying widely. Directly under the motor 29 is disposed a rotation axis 27. The rotation axis 27 and the output shaft of the motor 29 are linked to rotate the rotation axis 27 by the driving force of motor 29. Under the rotation axis 27, a socket 26, together with the road surface 34, for sandwiching a disk-shaped or cylindrical rubber sample 25 is connected. Thus, by the cooperation of the load cell 30, motor 29, and rotation axis 27, the downward load applied by the bellows 31 is transmitted to the rubber sample 25. Simultaneously, the rubber sample 25 is rotated on the road surface 34 as the rotation axis 27 rotates. In the vicinity of the rotation axis 27, a torque meter 28 is disposed to detect the torque generated by the rotation of the rubber sample 25.

[0038] The torque meter 28 and load cell 30 are electrically connected to a mensuration controlling trunk which is not shown so that the detected torque and loads are transmitted to the trunk. The mensuration controlling trunk is equipped with a control panel which displays the frictional force between the road surface 32 and rubber sample 25 calculated from the transmitted torque as well as the transmitted load data. The mensuration controlling trunk is also electrically connected to the aforementioned air source unit to control the load applied to the rubber sample 25 by regulating the air pressure supplied from the air source unit to the bellows 31 based on the load data transmitted from the load cell 30. The air source unit and the mensuration control trunk are electrically connected to an unillustrated generator.

[0039] The road surface friction test was performed using the above-described road surface friction tester under a load of 8 kgf and at a rotation speed of 20 rpm. The data obtained in the test (labo μ) were exponentially expressed based on the value of Comparative Example 1 (=100).

[0040] The values at 5° C and 20° C are indices representing friction coefficients on a wet road surface in a low temperature range and, on a wet road surface or a semi-wet road surface in a high temperature range, respectively. The greater these values, the better the evaluated gripping power.

[0041] The operational efficiency was evaluated by ranking the amounts of the rubber composition for tire treads adhered to the inner wall of the aforementioned mixer in 5 grades based on the total amount of the rubber composition charged in the mixer (5: almost no adhesion, 4: within 3%, 3: within 5%, 2: within 10%, 1: in excess of 10%). The greater the value, the better the evaluated operational efficiency.

[0042] The results are shown in Tables 1 and 2.

Table 1

	Comp. Ex.1A	Comp. Ex.2A	Comp. Ex.3A	Ex.1A	Ex.2A	Ex.3A
SBR*1	100	100	100	100	100	100
Carbon black*2	110	80	20	110	80	20
Silica*3	20	50	110	0 0 0		
Aluminium hydroxide*4	0	0	0	20	50	110
Clay*5	0	0	0	0	0	0
Total amount	130	130	130	130	130	130
Silane coupling agent*6	2	5	11	0	0	0
Acetone-Chloro-form extract	136	148	188	127	118	107
Aromatic oil	130	140	180	120	110	100
Resin A *7	0	0	0	0	0	0
Resin B *8	0	0	0	0	0	0

Table 1 (continued)

	Comp. Ex. 1A	Comp. Ex. 2A	Comp. Ex. 3A	Ex. 1A	Ex. 2A	Ex. 3A
Resin C *9	0	0	0	0	0	0
Vulcanization-accelerator (CZ)*10	1.9	1.9	1.9	1.9	1.9	1.9
Vulcanization-accelerator (TOT)*11	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
Labo μ index (5°C)	100	108	118	110	120	129
Labo μ index (20°C)	100	104	108	108	111	115
Index of operation-al efficiency	3	2	1	5	5	4

Table 2

	Ex. 4A	Ex. 5A	Ex. 6A	Ex. 7A
SBR*1	100	100	100	100
Carbon black*2	110	110	110	110
Silica*3	0	0	0	0
Aluminium hydroxide*4	0	20	20	20
Clay*5	20	0	0	0
Total amount	130	130	130	130
Silane coupling agent*6	0	0	0	0
Acetone-Chloro-form extract	127	126	126	125
Aromatic oil	120	90	90	90
Resin A *7	0	30	0	0
Resin B *8	0	0	30	0
Resin C *9	0	0	0	30
Vulcanization-accelerator (CZ)*10	1.9	1.9	1.9	1.9
Vulcanization-accelerator (TOT)*11	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5
Labo μ index (5°C)	105	112	109	113
Labo μ index (20°C)	104	111	113	117
Index of operation-al efficiency	5	4	5	4

Note)

Ex: Example

Comp. Ex.: Comparative Example

*1: 0120 (trademark), product of Japan Synthetic Rubber Co., Ltd. (styrene content: 35%)

*2: SAF (N₂SA 150 m²/g)

*3: Nipseal VN 3 AQ (trademark), product of Nippon Silica Co.

*4: Highdilite H-43M (trademark), product of Showa Denko Co., (average particle size: 0.6 μ m)*5: NUCAP 290 (trademark), product of J. M. Huber Co., (average particle size: 0.2 μ m)

*6: Si-69 (trademark), product of Degussa Co.

*7: C₉ aromatic petroleum resin, Neopolymer 80 (trademark), product of Nippon Petrochemical Co., Ltd. (softening point: 83° C)*8: C₉ aromatic petroleum resin, Neopolymer 140 (trademark), product of Nippon Petrochemical Co., Ltd. (softening point: 145° C)

*9: Alkylphenol resin, Phenolite AA1101 (trademark), product of Dainippon Ink and Chemicals, Inc. (softening point: 94° C)

*10: Noxella CZ-G (trademark product of Ohuchi Sinko Chemical Industry Co. N-cyclohexyl-2-benzothiazyl-1-sulfenamide)

*11: Noxella TOT-N (trademark product of Ohuchi Sinko Chemical Industry Co. tetrakis-2-ethylhexylthiuram di-sulfide)

[0043] When the results of Example 1A and Comparative Example 1A, those of Example 2A and Comparative Ex-

ample 2A, and those of Example 3A and Comparative Example 3A are compared in pairs, it is understood that the data obtained in Examples 1A, 2A, and 3A, where the amount of carbon black and that of silica or the powdery inorganic compound (aluminium hydroxide) were the same as those used in the corresponding Comparative Examples but aluminium oxide was used instead of silica, are superior to Comparative Examples with respect to the labo μ values at 5° C (low temperature range) and 20° C (high temperature range) and the operational efficiency.

[0044] It is also noteworthy that when the results of Example 4A in which clay was employed as the powdery inorganic compound are compared with those of Comparative Example 1A, in which the amount of carbon black and that of silica or the powdery inorganic compound were the same as those used in Example 4A, improved labo μ values at 5° C (low temperature range) and 20° C (high temperature range) and improved operational efficiency were obtained in Example 4A. Moreover, comparison between Example 1A and Example 4A, where the amount of carbon black and that of the powdery inorganic compound employed were common, revealed that Example 1A (in which aluminium hydroxide was employed as the powdery inorganic compound) exhibited a greater improvement in the labo μ values at 5° C (low temperature range) and 20° C (high temperature range).

[0045] The samples of Examples 5A and 6A contained a C₉ aromatic petroleum resin. When the results of these examples are compared with those of Comparative Example 1A, in which the amount of carbon black and that of silica or the powdery inorganic compound are common, it is understood that the labo μ values at 5° C (low temperature range) and 20° C (high temperature range) and operational efficiency were improved. Furthermore, when the results of Examples 1A, 5A, and 6A are compared to each other, it is understood that Examples 5A and 6A, in which a C₉ aromatic petroleum resin was used, exhibited a greater enhancement in the labo μ value at 20° C (high temperature range).

[0046] The sample of Example 7A contained an alkylphenol resin. When the results of this example are compared with those of Comparative Example 1A, in which the amount of carbon black and that of silica or the powdery inorganic compound were common, it is understood that the labo μ values at 5° C (low temperature range) and 20° C (high temperature range) and operational efficiency were improved. Especially, the labo μ value at 20° C (high temperature range) was remarkably improved.

Examples 1B to 9B and Comparative Example 1B:

[0047] The components (amounts expressed as parts by weight) shown in Tables 3 and 4 were kneaded to prepare various rubber compositions for tire treads. Also, a road surface friction test was conducted in the same manner as that described hereinbefore.

[0048] Concerning abrasion resistance, a test was performed using a Ranbone-type friction tester at room temperature and at a slip ratio of 25%, and the results were exponentially expressed based on the value obtained in Comparative Example 1B. The greater the abrasion resistance index, the better the evaluated abrasion resistance.

[0049] The results are shown in Tables 3 and 4.

Table 3

	Comp. Ex.1B	Ex.1B	Ex.2B	Ex.3B	Ex.4B
SBR*1	100	100	100	100	100
Carbon black*2	80	80	80	80	80
Silica*3	70	50	50	50	50
Aluminium hydroxide*4	0	20	60	100	0
Clay*5	0	0	0	0	20
Total amount	150	150	190	230	150
Silane coupling agent*6	7	5	5	5	5
Acetone-Chloro-form extract	178	128	147	168	127
Aromatic oil	170	120	140	160	120
Resin A *7	0	0	0	0	0
Resin B *8	0	0	0	0	0
Resin C *9	0	0	0	0	0
Vulcanization-accelerator (CZ)*10	1.9	1.9	1.9	1.9	1.9
Vulcanization-accelerator (TOT)*11	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5
Labo μ index (5°C)	100	109	113	118	104
Labo μ index (20°C)	100	108	111	114	104

Table 3 (continued)

	Comp. Ex.1B	Ex.1B	Ex.2B	Ex.3B	Ex.4B
Abrasion resistance	100	105	104	103	103

Table 4

	Ex.5B	Ex.6B	Ex.7B	Ex.8B	Ex.9B
SBR*1	100	100	100	100	100
Carbon black*2	80	80	80	80	80
Silica*3	50	50	50	50	50
Aluminium hydroxide*4	20	20	20	20	20
Clay*5	0	0	0	0	0
Total amount	150	150	150	150	150
Silane coupling agent*6	5	5	5	0	0
Acetone-Chloro-form extract	126	126	125	127	126
Aromatic oil	90	90	90	120	90
Resin A *7	30	0	0	0	0
Resin B *8	0	30	0	0	30
Resin C *9	0	0	30	0	0
Vulcanization-accelerator (CZ)*10	1.9	1.9	1.9	1.9	1.9
Vulcanization-accelerator (TOT)*11	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5
Labo μ index (5°C)	111	108	112	110	109
Labo μ index (20°C)	111	113	117	106	111
Abrasion resistance	104	107	104	100	112
Note) *1 to *11: See the notes under Table 2.					

[0050] When the results of Example 1B and Comparative Example 1B are compared, Example 1B, in which aluminium hydroxide was employed as the powdery inorganic compound, exhibited enhanced labo μ values at 5° C (low temperature range) and 20° C (high temperature range) and abrasion resistance although the amount of carbon black and the total amount of carbon black and silica and/or the powdery inorganic compound were common.

[0051] The samples of Examples 2B and 3B were prepared by varying the amount of aluminum hydroxide of Example 1B. From the results, it is understood that the labo μ values at 5° C (low temperature) and 20° C (high temperature range) were further improved compared to the sample of Example 1B.

[0052] When the results of Example 4B and Comparative Example 1B are compared, Example 4B, in which clay was employed as the powdery inorganic compound, exhibited enhanced labo μ values at 5° C (low temperature range) and 20° C (high temperature range) and abrasion resistance although the amounts of carbon black and the total amounts were common. Moreover, when the data of Example 4B is compared with Example 1B, in which aluminium hydroxide was used as the powdery inorganic compound, Example 1B exhibited highly enhanced labo μ values at 5° C (low temperature range) and 20° C (high temperature range). This reveals that aluminium hydroxide is more preferable than clay as the powdery inorganic compound.

[0053] The samples of Examples 5B and 6B contained a C₉ aromatic petroleum resin. When they are compared with Comparative Example 1B, in which the amount of carbon black and the total amount were common, it is understood that the labo μ values at 5° C (low temperature range) and 20° C (high temperature range) and abrasion resistance were improved. Moreover, comparison of Example 1B versus Examples 5B and 6B reveals that the samples of Examples 5B and 6B, which contained a C₉ aromatic petroleum resin, exhibited a greater improvement in the labo μ value at 20° C (high temperature) than Example 1B although in these examples, the amount of carbon black, that of the powdery inorganic compound and that of silica were common.

[0054] The sample of Example 7B contained an alkyl phenol resin. When the results of this example are compared with those of Comparative Example 1B, in which the amount of carbon black and the total amount were common to those of Example 7B, it is found that the labo μ values at 5° C (low temperature) and 20° C (high temperature range) and abrasion resistance were improved. Especially, the labo μ value at 20° C (high temperature range) was remarkably improved.

[0055] Example 8B was different from other examples in that it did not contain a silane coupling agent. When the results of Example 8B are compared to those of Example 1B, in which the amount of carbon black, that of powdery inorganic compound, and that of silica were identical to those of Example 8B, it is found that the labo μ value at 20° C (high temperature range) and abrasion resistance decreased. However, when the results of Example 8B are compared to those of Comparative Example 1B, in which the amount of carbon black and the total amount were identical to those of Example 8B, it is found that the labo μ values at 5° C (low temperature range) and 20° C (high temperature range) were improved although the abrasion resistance stayed almost the same. From these results, it is understood that use of a silane coupling agent is more preferable.

[0056] However, comparison between Examples 9B and 6B shows that if a resin is used, similar effects can be obtained regardless of the absence of a silane coupling agent.

[0057] As described above, the rubber compositions for tire treads according to the present invention remarkably improve the gripping power on wet and semi-wet road surfaces which are not only in a low temperature range but also in a high temperature range, without adversely affecting the abrasion resistance.

Claims

1. A rubber composition for tire treads **characterized by** comprising:

a rubber component containing at least 70 parts by weight of a styrene-butadiene rubber whose styrene content is 20 to 60%; and further comprising, based on 100 parts by weight of the rubber component:
5 to 150 parts by weight of a powdery inorganic compound represented by the following formula (I) and having a particle size from 0.01 to 10 μm :



in which M^1 is at least one selected from the group consisting of Al, Mg, Ti, and Ca; any oxide of any one of the metals; or any hydroxide of any one of the metals; and m, x, y, and z are integers from 1 to 5, 0 to 10, 2 to 5, and 0 to 10, respectively;

5 to 170 parts by weight of carbon black having a nitrogen adsorption specific area of 80 to 280 m^2/g so that the total amount of the powdery inorganic compound and the carbon black falls in the range of 70 to 200 parts by weight;

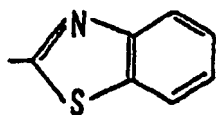
5 to 140 parts by weight of silica having a nitrogen adsorption specific area of 130 to 280 m^2/g , wherein the total amount of the powdery inorganic compound and the silica and the carbon black falls in the range of 80 to 250 parts by weight based on 100 parts by weight of the overall rubber component;

the amount of an extract obtained by extracting the rubber composition after being vulcanized from acetone and chloroform being 30 to 270 parts by weight, based on 100 parts by weight of the rubber component.

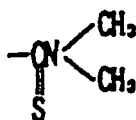
2. A rubber composition as claimed in claim 1, **characterized by** further comprising a silane coupling agent in an amount of 3 to 20% by weight based on the amount of the silica.

3. A rubber composition as claimed in claim 1, **characterized by** further comprising 3 to 50 parts by weight of at least one of a C_9 -aromatic petroleum resin and an alkylphenol resin.

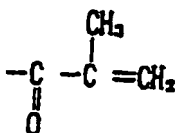
4. A rubber composition as claimed in claim 2, **characterized in that** the silane coupling agent is a compound represented by the formula $\text{Y}_3\text{-Si-C}_n\text{H}_{2n}\text{A}$, wherein Y is $\text{C}_1\text{-C}_4$ alkyl, alkoxy, or a chlorine atom and the three Y's may be the same or different from each other, n is an integer from 1 to 6 inclusive, A is $\text{-S}_m\text{C}_n\text{H}_{2n}\text{Si-Y}_3$, nitroso, mercapto, amino, epoxy, vinyl, a chlorine atom, imido, or $\text{-S}_m\text{Z}$ wherein m is an integer from 1 to 6 inclusive, n and Y are as defined hereinabove, and Z is a group selected from the compounds (A), (B), and (C):



(A)



(B)



(C)

5. A rubber composition as claimed in any of claims 1 to 4,
characterized in that the powdery inorganic compound of formula (I) is aluminium hydroxide.

Patentansprüche

1. Kautschukzusammensetzung für Reifenlaufflächen, dadurch gekennzeichnet, dass sie:

eine Kautschukkomponente umfasst, die wenigstens 70 Gew.-Teile eines Styrol-Butadien-Kautschuks enthält, dessen Styrolgehalt 20 bis 60 % beträgt; und dass sie ferner auf Basis von 100 Gew. -Teilen der Kautschukkomponente umfasst:

5 bis 150 Gew.-Teile einer pulverförmigen anorganischen Verbindung, die durch die folgende Formel (I) dargestellt wird und eine Teilchengröße von 0,01 bis 10 µm hat:



worin M^1 wenigstens ein Vertreter ist, der aus der Gruppe ausgewählt ist, die aus Al, Mg, Ti und Ca besteht; ein beliebiges Oxid eines beliebigen der Metalle; oder ein beliebiges Hydroxid eines beliebigen der Metalle; und m, x, y, und z ganze Zahlen von 1 bis 5, 0 bis 10, 2 bis 5 bzw. 0 bis 10 sind;

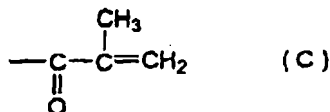
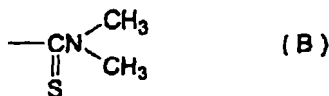
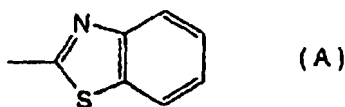
5 bis 170 Gew.-Teile Russ mit einer spezifischen Stickstoff-Adsorptionsfläche von 80 bis 280 m²/g, so dass die Gesamtmenge der pulverförmigen anorganischen Verbindung und des Russes in den Bereich von 70 bis 200 Gew.-Teile fällt;

5 bis 100 Gew.-Teile Kieselerde mit einer spezifischen Stickstoff-Adsorptionsfläche von 130 bis 280 m²/g, worin die Gesamtmenge der pulverförmigen anorganischen Verbindung und der Kieselerde und des Russes in den Bereich von 80 bis 250 Gew.-Teile auf Basis von 100 Gew.-Teilen der gesamten Kautschukkomponente fällt;

wobei die Menge des Extrakts, der durch Extrahieren der Kautschukzusammensetzung nach Vulkanisation aus

Aceton und Chloroform erhalten wird, 30 bis 270 Gew.-Teile auf Basis von 100 Gew.-Teilen der Kautschukkomponente ist.

2. Kautschukzusammensetzung gemäss Anspruch 1, **dadurch gekennzeichnet, dass** sie ferner einen Silankuppler in einer Menge von 3 bis 20 Gew.% auf Basis der Kieselerdemenge umfasst.
3. Kautschukzusammensetzung gemäss Anspruch 1, **dadurch gekennzeichnet, dass** sie ferner 3 bis 50 Gew.-Teile wenigstens eines Vertreters aus einem aromatischen C₉-Petroleumharz und einem Alkylphenolharz umfasst.
4. Kautschukzusammensetzung gemäss Anspruch 2, **dadurch gekennzeichnet, dass** der Silankuppler eine durch die Formel Y₃-Si-C_nH_{2n}A dargestellte Verbindung ist, worin Y C₁₋₄-Alkyl, Alkoxy oder ein Chloratom ist und die drei Y-Gruppen gleich oder verschieden voneinander sein können, n eine ganze Zahl von 1 bis einschliesslich 6 ist, A -S_mC_nH_{2n}Si-Y₃, Nitroso, Mercapto, Amino, Epoxy, Vinyl, ein Chloratom, Imido oder -S_mZ ist, worin m eine ganze Zahl von 1 bis einschliesslich 6 ist, n und Y wie zuvor definiert sind und Z eine aus den Verbindungen (A), (B) und (C) ausgewählte Gruppe ist:



5. Kautschukzusammensetzung gemäss einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** die pulverförmige anorganische Verbindung der Formel (I) Aluminiumhydroxid ist.

Revendications

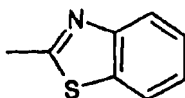
1. Composition de caoutchouc pour bande de roulement de pneus, **caractérisée en ce qu'elle comprend** :

- un composé de caoutchouc contenant au moins 70 parties en poids d'un caoutchouc styrène-butadiène dont la teneur en styrène est de 20 à 60 % ; et comprenant de plus, sur la base de 100 parties en poids de composés de caoutchouc ;
- 5 à 150 parties en poids d'un composé inorganique poudreux représenté par la formule (I) suivante et ayant une taille de particules de 0,01 à 10 µm :

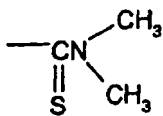


dans laquelle M¹ est au moins une fois choisi parmi le groupe consistant en Al, Mg, Ti et Ca ; n'importe quel oxyde de n'importe lequel de ces métaux ; ou n'importe quel hydroxyde de n'importe lequel de ces métaux ; et m, x, y et z sont des entiers de 1 à 5, 0 à 10, 2 à 5, et 0 à 10 respectivement ;

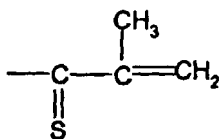
- 5 à 170 parties en poids de noir de carbone ayant une aire d'absorption spécifique en azote de 80 à 280 m²/g, de sorte que la quantité totale de composé inorganique poudreux et du noir de carbone tombe dans l'intervalle de 70 à 200 parties en poids ;
 - 5 à 100 parties en poids de silice ayant une aire d'adsorption spécifique en azote de 130 à 280 m²/g, dans laquelle la quantité totale de composé inorganique poudreux et de silice et de noir de carbone tombe dans l'intervalle de 80 à 250 parties en poids sur la base de 100 parties en poids de la totalité du composé de caoutchouc ;
 - la quantité d'un extrait obtenu par extraction de la composition de caoutchouc après vulcanisation dans l'acétone et de chloroforme étant de 30 à 270 parties en poids, sur la base de 100 parties en poids de composé de caoutchouc.
2. Composition de caoutchouc selon la revendication 1, **caractérisée en ce qu'elle** comprend de plus un agent de couplage de silane dans une quantité de 3 à 20 % en poids sur la base de la quantité de silice.
3. Composition de caoutchouc selon la revendication 1, **caractérisée en ce qu'elle** comprend de plus 3 à 50 parties en poids d'au moins une résine de pétrole aromatique en C₉ et une résine d'alkylphénol.
4. Composition de caoutchouc selon la revendication 2, **caractérisée en ce que** l'agent de couplage de silane est un composé représenté par la formule Y₃-Si-C_n-H_{2n}A, dans laquelle Y est un alkyle en C₁-C₄, alkoxy, ou un atome de chlore et les trois Y peuvent être identiques ou différents les uns des autres, n est un entier de 1 à 6 inclus, A est -S_mC_nH_{2n}Si-Y₃, nitroso, mercapto, amino, epoxy, vinyle, un atome de chlore, imido ou -S_mZ dans laquelle m est un entier de 1 à 6 inclus, n et Y sont tels que définis ci-dessus, et Z est un groupe choisi parmi les composés (A), (B) et (C) :



(A)



(B)



(C)

5. Composition de caoutchouc selon une quelconque des revendications 1 à 4, **caractérisée en ce que** le composé inorganique poudreux de la formule (I) est l'hydroxyde d'aluminium.

FIG. 1

